



MEMORANDUM

To: Mr. Dana Bayuk – Oregon DEQ Date: January 17, 2011

From: James G.D. Peale, RG Project: 8128.01.20

RE: ISCR-Enhanced Bioremediation Performance Monitoring Data Submittal
DNAPL and Groundwater Data – WS-33-81
Siltronic Corporation – ECSI #183

The following summarizes data and trends from Group 2 performance monitoring well (PMW) WS-33-81 using data received through October 31, 2010. The data include results for volatile organic compound (VOC) and semi-VOC (SVOC) analyses of dense, non-aqueous phase liquid (DNAPL) characteristic of manufactured gas plant (MGP) operations collected from this PMW at the request of the Oregon Department of Environmental Quality (DEQ)¹. The data also include results for VOC analyses of groundwater from this PMW. The data from the sampling were compared to data from the desorption bench test, as reported to DEQ in the Desorption Bench Test Report (DBTR) on June 26, 2007.

The results indicate the following:

- Degradation of trichloroethene (TCE) in the aqueous phase results in removal of TCE from the non-aqueous phase, most likely via desorption driven by the concentration differential (gradient) between the two phases.
- The removal of TCE from the non-aqueous phase is approximately 3x faster than the aqueous phase degradation rate.
- The average *in situ* rate of reduction of TCE in the non-aqueous phase (i.e., the TCE desorption rate) is much faster than the desorption rate measured during the desorption bench test.

These data continue to suggest that desorption enhanced by aqueous phase degradation is an effective mechanism for removing TCE and its degradation products from the non-aqueous phase (regardless of type) present at the site. The following sections describe the data and methods used to develop this conclusion.

¹ In response to a request regarding EIB data, an MS Excel worksheet including the DNAPL analytical data was submitted under separate cover to DEQ on January 13, 2011.

BACKGROUND

MGP DNAPL has been observed in the subsurface throughout the portion of the Siltronic property impacted by TCE and its degradation products, both in boring logs and monitoring wells. In some locations (e.g., WS-11-125), concentrations of TCE in the non-aqueous phase (either sorbed to soil or in MGP DNAPL, and referred to as TCE_{NA}) are orders of magnitude greater than the measured aqueous phase concentrations. Aqueous phase TCE concentrations (in excess of 1 per cent of the solubility limit) suggest the presence of TCE_{NA} , as do mass balance calculations using chloride data from the source area PMWs. As noted in the DBTR, the presence of TCE_{NA} could possibly reduce the effectiveness of the combined *in situ* chemical reduction (ISCR) and bioremediation (collectively, ISCR-enhanced bioremediation) of aqueous phase TCE. Field data indicate that the presence of TCE_{NA} in the vicinity of WS-33-81 does not appear to have significant impact on the effectiveness of ISCR-enhanced bioremediation of TCE.

The results described in the DBTR confirmed that the combination of desorption and degradation removes TCE and its degradation products from MGP DNAPL. During installation of Group 2 PMW WS-33-81, the presence of MGP DNAPL was noted during boring, and subsequent measurements confirmed collection of MGP DNAPL in the well. DEQ directed Siltronic to incorporate MGP DNAPL sampling into the performance monitoring program. The coordinated sampling of MGP DNAPL and groundwater provided the data needed to field test the results described in the DBTR.

ANALYTICAL DATA

Starting in February 2009, groundwater samples were collected from WS-33-81 consistent with the DEQ-approved sampling schedule. Samples were collected throughout the injection period and bimonthly starting in August 2009, and submitted to Specialty Analytical of Clackamas, Oregon (SA) for VOC analysis by USEPA Method 8260. While additional parameters are important for the performance monitoring, the discussion herein is limited to the VOC analyses of groundwater and MGP DNAPL.

Starting in July 2009, MGP DNAPL samples were collected from WS-33-81 when monthly water level monitoring detected the presence of MGP DNAPL. MGP DNAPL samples were decanted from a single-use bailer into laboratory-supplied glass jars and submitted to SA for VOC analysis by USEPA Method 8260.¹

RESULTS

The analytical results for TCE and its degradation products in MGP DNAPL and groundwater are summarized in Table 1 and shown on Figure 1. The aqueous phase TCE concentrations have decreased significantly (and below the remedial action objective, or RAO, for the source area); cis-1,2-DCE concentrations are generally unchanged, and vinyl chloride concentrations have increased

¹ Additional analyses were conducted contingent upon sample volume, and included SVOCs (USEPA 8270), viscosity, water content, TPH-Gx/Dx, total organic carbon, and specific gravity.

but are much lower than the cis-1,2-DCE concentrations. These results are consistent with the Group 1 and 2 PMWs (Figure 2)¹.

In the non-aqueous phase, the much greater TCE_{NA} concentrations have also declined significantly, with TCE not detected above the method reporting limit (MRL) in the most samples collected since May 2010 (except for August 2010). Cis-1,2-DCE concentrations have declined somewhat, with some variability in the data, and vinyl chloride concentrations have increased slightly.

Figure 3 shows the change in TCE_{NA} vs. TCE in the aqueous phase, using log(*e*) concentrations. The data are fitted with linear trends in order to compare the removal rate (i.e., the slope of the linear trend). The slope for the TCE_{NA} data (and therefore the removal rate) is approximately 3x greater than for TCE in the aqueous phase. As shown on Table 2, the TCE_{NA} removal rate (*r*) for the period of July 2009 through May 2010 was 11,832 ug/day, or 493 ug/hr. This rate is 400x higher than the rate reported in the DBTR (approximately 1.2 ug/hr).

As noted in the DBTR, the change in the rate of TCE desorption was positively correlated with the change in concentration gradient – i.e., as the gradient decreased, the rate decreased. This observation is consistent with accepted understanding of sorption/desorption kinetics. The data from WS-33-81 confirm this relationship. The concentration gradient is expressed as the log of the NAPL-water distribution coefficient (*k_{nw}*), where:

$$k_{nw} = \text{TCE}_{NA} / \text{TCE}$$

From this equation, it is clear that larger *k_{nw}* values represent steeper concentration gradients between the two phases; decreasing *k_{nw}* values are expected as concentrations in the two phases approach each other or in this case, non-detect values. Figure 4 shows the log(*k_{nw}*) and log(*r*) data. The data show a coincident decline in the gradient and removal rate. Assuming that most of the TCE_{NA} removal is due to desorption (i.e., as opposed to dechlorination in the non-aqueous phase), the data suggest that the concentration gradient is driving the desorption of TCE from the non-aqueous phase to the aqueous phase, where dechlorination occurs.

DISCUSSION

TCE

The results are encouraging and clearly support the application of ISCR-enhanced bioremediation for the TCE source area. The data indicate that desorption from the non-aqueous phase is the result of the concentration gradient created by accelerated dechlorination in the aqueous phase. Similar concentration gradients could be expected between any non-aqueous phase and the aqueous phase. In this case, there are multiple potential non-aqueous phases: TCE sorbed into MGP DNAPL (documented); TCE sorbed to the organic carbon fraction of soil (suspected but not documented);

¹ Figure 2 shows Environmental Visualization System (EVS) mass estimates of the total moles (*M*) of TCE, cis-1,2-DCE, and vinyl chloride in the source area.

or TCE as NAPL (suspected but not observed). Since the concentration gradient is not unique to the type of non-aqueous phase, the mechanism for dissolution or desorption from a non-aqueous phase into an aqueous phase is not unique. Based on the results, non-aqueous phase TCE (regardless of type) is effectively remediated by ISCR-enhanced bioremediation.

The TCE degradation rate in the aqueous phase (slope shown on Figure 3) incorporates the influx of TCE from the non-aqueous phase. Absent the contribution of TCE from the non-aqueous phase, degradation in the aqueous phase would likely be occurring more quickly than observed. However, the aqueous phase removal rates for TCE are satisfactory, with concentrations below the injection threshold since March 2009.

Cis-1,2-DCE and Vinyl Chloride

As noted above, Table 1 includes data for the primary degradation products (cis-1,2-DCE and vinyl chloride) in the non-aqueous and aqueous phases. The aqueous phase concentrations of cis-1,2-DCE have not changed significantly during the monitoring period; the non-aqueous phase concentrations are still elevated but have declined by an order of magnitude. The vinyl chloride concentrations in both phases have increased but are significantly lower than the cis-1,2-DCE concentrations. Both data sets are highly variable, and reflect exchanges between the aqueous and non-aqueous phases. Unlike the TCE data, the degradation product data reflect contribution from parent product degradation, which at this time prevents a clear interpretation of desorption and degradation relationship.

Based on the pilot study data and data from other Group 1 and 2 PMWs (e.g., WS-31-106, WS-37-51, WS-33-106), aqueous phase concentrations of cis-1,2-DCE and vinyl chloride in WS-33-81 are expected to decrease once TCE is sufficiently depleted. Because desorption kinetics are not unique to TCE, the decrease in the aqueous phase of the degradation products will increase the concentration gradient between the two phases. As the concentration gradient increases for these compounds, desorption rates are expected to increase, resulting in reduced non-aqueous phase concentrations of the daughter products.

SUMMARY

Investigation data suggested the presence of TCE DNAPL, and subsequent monitoring confirmed the presence of TCE sorbed into non-aqueous phases (e.g., MGP DNAPL or sorbed to soil). Dissolution from these non-aqueous phases contributes to the mass of TCE and its degradation products in the dissolved phase. The mechanisms resulting from ISCR-enhanced bioremediation are effective in the dissolved phase, but have not been documented for the non-aqueous phase.

Data from WS-33-81 suggest that degradation of TCE in the aqueous phase has effected similar and more rapid decreases of TCE in the non-aqueous phase (MGP DNAPL). TCE was not detected in the most recent MGP DNAPL samples; similarly, aqueous phase TCE concentrations are well below the injection threshold (11,000 ug/L) and are most recently below the Joint Source Control Strategy Screening Level Value (30 ug/L).

Removal of TCE from the MGP DNAPL is likely occurring via desorption (from the non-aqueous phase to the aqueous phase) coupled with aqueous phase degradation. Desorption rates are driven by the concentration gradient between the non-aqueous and aqueous phases, regardless of the type of non-aqueous phase, such that removal of TCE from the aqueous phase will effect rapid desorption of TCE from MGP DNAPL, TCE NAPL, or TCE sorbed to soil organic carbon. Because desorption is also not compound-specific, predicted (but as yet not observed) aqueous phase decreases in TCE degradation products are expected to effect similar reductions in the non-aqueous phase.

The data indicate that ISCR-enhanced bioremediation as implemented in the source area will effectively remove TCE and its degradation products from groundwater, regardless of the potential for these compounds to be present in a non-aqueous phase.

Attachments: Tables
Figures

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TABLES



Table 1
TCE and its Degradation Products
Groundwater and MGP DNAPL Data
Siltronic Corporation
Portland, OR

DATE	TCE (ug/l)	cis-1,2-DCE (ug/l)	trans-1,2-DCE (ug/l)	1,1-DCE (ug/l)	Vinyl chloride (ug/l)
Feb-09	21,400	81,600	953	258	79
Mar-09	4,990	135,000	806	174	86
May-09	496	148,000	1,080	55	147
Jul-09	1,150	106,000	1,060	288	738
Aug-09	1,100	128,000	752	222	999
Oct-09	431	104,000	704	214	4,130
Dec-09	92	126,000	465	120	3,720
Feb-10	160	158,000	816	201	8,890
Apr-10	65	108,000	594	216	9,590
Jun-10	24	126,000	456	131	14,300
Aug-10	19.9	60,900	473	133	20,300
Oct-10	14.4	99,800	476	107	14,200
DATE	TCE (ug/kg)	cis-1,2-DCE (ug/kg)	trans-1,2-DCE (ug/kg)	1,1-DCE (ug/kg)	Vinyl chloride (ug/kg)
Jul-09	3,480,000	3,500,000	14,300	15,500	1,430
Sep-09	2,850,000	3,860,000	29,400	13,200	2,170
Oct-09	2,570,000	3,500,000	16,500	12,500	3,590
Nov-09	4,200,000	5,940,000	23,100	18,200	6,890
Dec-09	155,000	736,000	<12500	<12500	<12500
Jan-10	141,000	565,000	<2500	<2500	<2500
Feb-10	6,510	154,000	<500	<500	<500
Mar-10	9,940	645,000	3,560	<2500	2,900
Apr-10	6,480	1,180,000	3,080	500	2,690
May-10	<2500	1,560,000	6,770	<2500	<2500
Jun-10	<2500	1,580,000	5,340	<2500	4,780
Jul-10	<2500	1,000,000	<2500	<2500	5,970
Aug-10	1,760	2,540,000	14,000	4,670	17,300
Sep-10	<2500	1,390,000	5,020	<2500	6,600
Oct-10	<2500	572,000	<2500	<2500	<2500

< indicates compound not detected above the reporting limit

Table 2
TCE Gradients and Removal Rates
MGP DNAPL Data - WS-33-81
Siltronic Corporation
Portland, OR

TCE-Aq		TCE-NA		Distribution Coefficient		TCE Removal Rate	
Sample Date	(ug/l)	Sample Date	(ug/kg)	Knw	Log Knw	Rate	Log Rate
Jul-09	1,150	Jul-09	3,480,000	3,026	3.48		
Aug-09	1,100	Sep-09	2,850,000	2,591	3.41	10,500	4.02
Oct-09	431	Oct-09	2,570,000	5,963	3.78	15,556	4.19
Interpolated	262	Nov-09	4,200,000	16,055	4.21	-95,882	
Dec-09	92	Dec-09	155,000	1,681	3.23	43,125	4.63
Interpolated	126	Jan-10	141,000	1,118	3.05	359	2.56
Feb-10	160	Feb-10	6,510	41	1.61	4,803	3.68
Interpolated	112	Mar-10	9,940	88	1.95	-95	
Apr-10	65	Apr-10	6,480	100	2.00	173	2.24
Interpolated	45	May-10	1,250	28	1.45	141	2.15
Jun-10	24	Jun-10	1,250	51	1.71		

Removal rate	11,832 ug/day 493 ug/hr
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Aq - Aqueous phase

NA - non-aqueous phase

Interpolated - average of prior and following data

italic indicates TCE not detected; value shown is 1/2 method reporting limit

Knw - NAPL-water distribution coefficient

Not calculated

Removal rate not calculated after June 2010 due to continuing ND results in NAPL

FIGURES



Figure 1
TCE, cDCE and VC in Groundwater and MGP DNAPL
WS-33-81

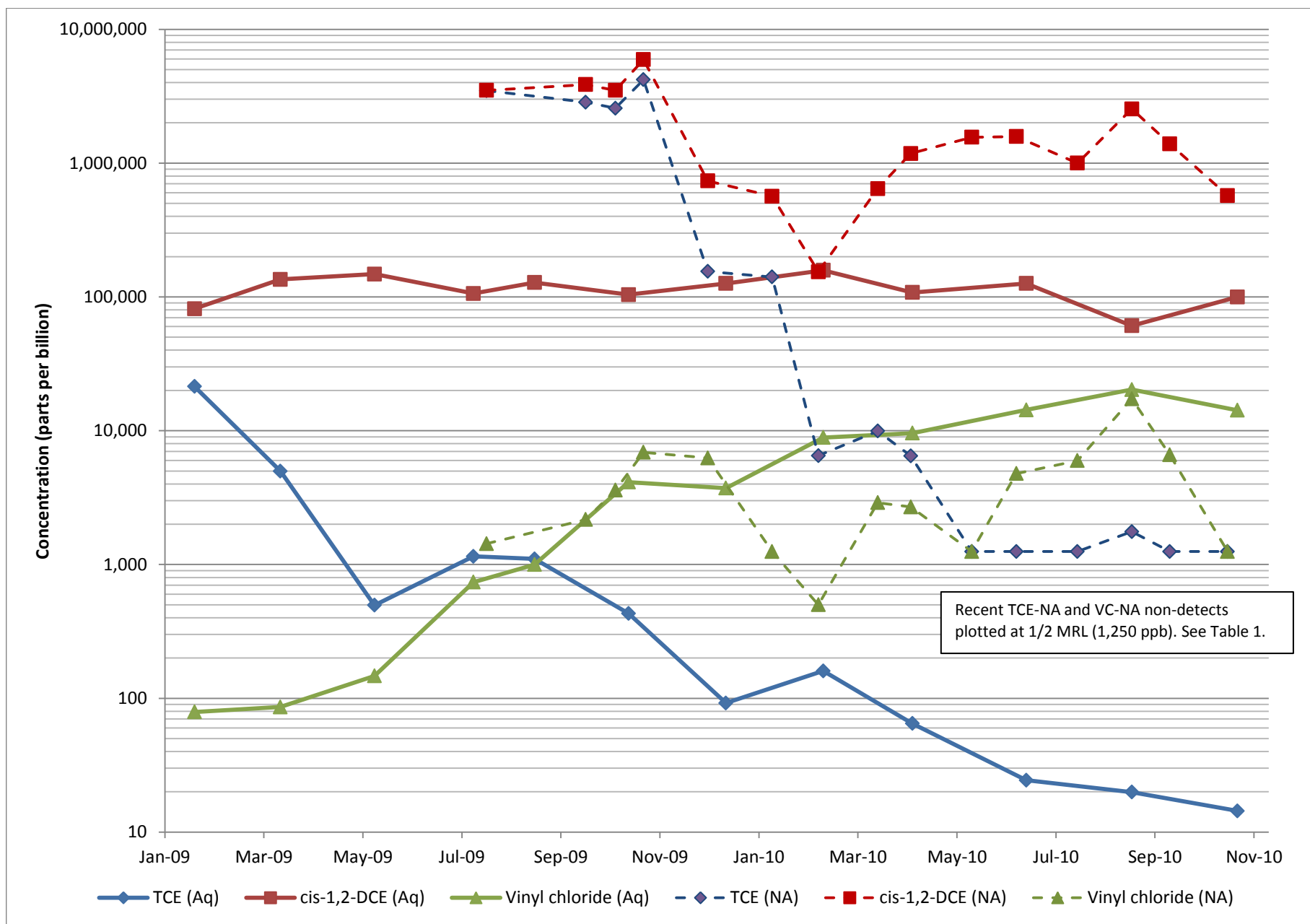


Figure 2
EVS Mass Estimates for Source Area
Group 1 and 2 PMWs

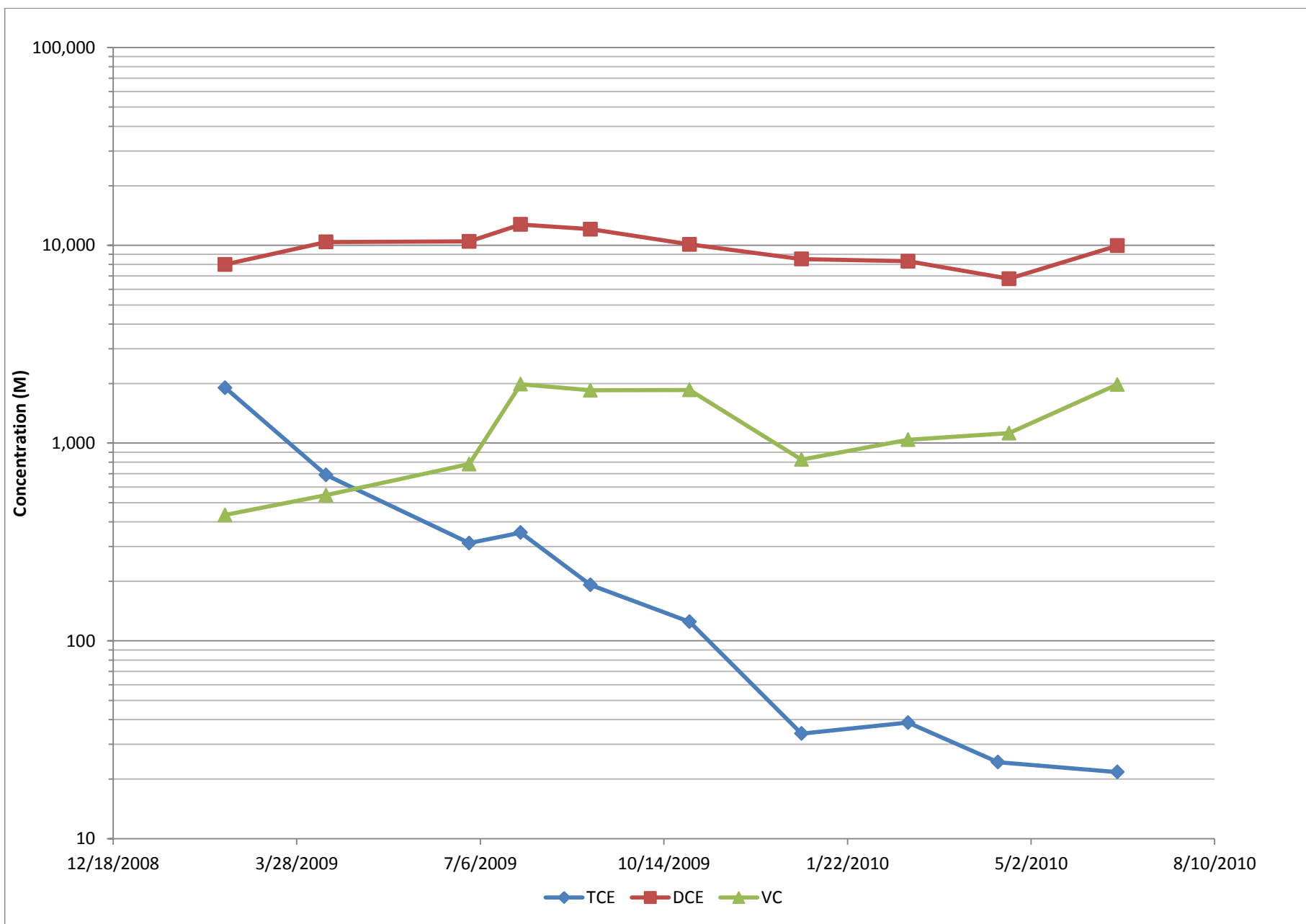


Figure 3
TCE in Groundwater (ug/L) and MGP DNAPL (ug/kg)
WS-33-81

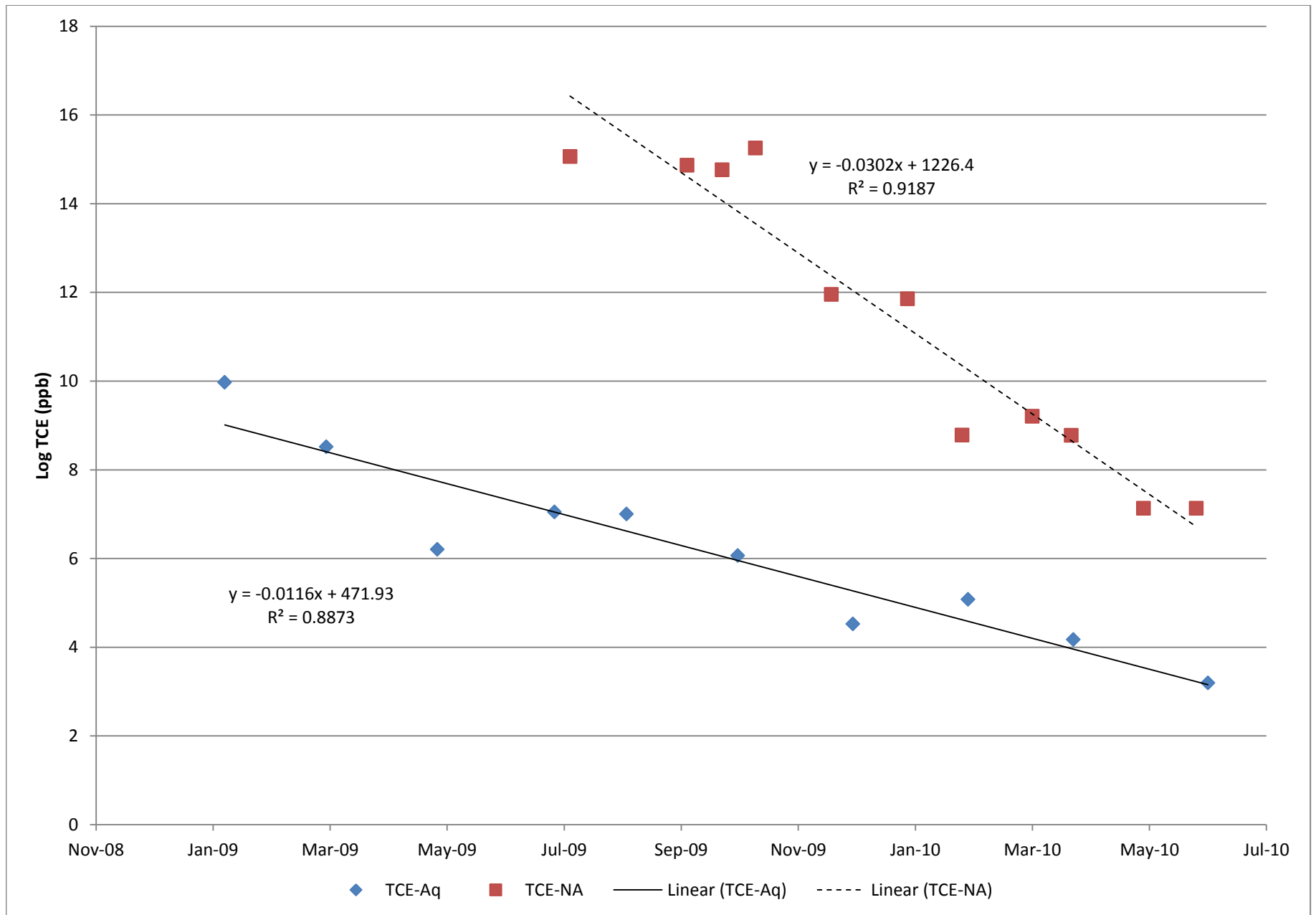


Figure 4
Change in TCE Gradient and Removal Rate
WS-33-81

